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NONAQUEOUS ELECTROLYTE BATTERY

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Inventors	Osamu Furukawa c/o Sanyo Electric Co., Ltd. 2-18 Keihan Dori, Moriguchi City Kazuo Moriwake Address same as above
Applicant	Sanyo Electric Co., Ltd. 2-18 Keihan Dori, Moriguchi City
Agent	Attorney Shizuo Sano

SPECIFICATIONS

1. Title of Invention

Nonaqueous electrolyte battery

2. Claim

(1) Nonaqueous electrolyte battery, characterized in that it is a nonaqueous electrolyte battery comprised of a negative electrode which has active material in the form of a light metal such as lithium or sodium, a positive electrode active material in the form of a metal oxide, sulfide, or halogen compound, and a nonaqueous electrolyte solution consisting of at least one solvent and one solute in which expanded graphite is used as the electrically conducting material of the positive electrode.

3. Detailed Explanation of Invention

This invention relates to a nonaqueous electrolyte battery which is comprised of a negative electrode with a light metal active material such as sodium, lithium, or magnesium, a positive electrode with active material such as a metal oxide, sulfide, or halogen compound, and a nonaqueous electrolyte solution.

The positive electrode of this type of battery is usually constructed with the addition of an electrically conducting material and a binder. In addition, the electrically conducting material usually also serves as a liquid retention medium because of which acetylene black or synthetic graphite has been used very frequently.

The inventors directed pointed research on this electrically conducting material as a result of which they discovered that the use of expanded graphite will introduce spectacular improvement in the battery properties.

What is referred to as expanded graphite is prepared by subjecting graphite to the following treatment.

As illustrated in Fig. 1, graphite consists of hexagonally shaped flat crystals of the hexagonal crystal system and possesses a layer shaped structure in which these hexagonal element rings are strung together. When this graphite is subjected to a wet oxidation using an oxidizing medium such as a mixture of concentrated sulfuric and nitric acids or acid with potassium chlorate, potassium dichromate, or potassium permanganate and then quick heating this wet oxidation product at a high temperature of above 900°C, the layer structure described above is expanded 50-1,000 times in the C axial direction.

The expanded graphite which has undergone such a treatment is thermodynamically stable and consists of a porous particle structure of high electrical conductivity, and it possesses extremely good pressure forming property.

Consequently, the use of expanded graphite in a finely divided state as electrically conducting material will result in a positive electrode which has this expanded graphite distributed uniformly throughout the positive electrode to provide greatly increased contact surface with the positive electrode active material and greatly improve the electrical conductance and liquid retention properties of the positive electrode. At the same time, good pressure forming property is acquired as a result of

which the addition of a binder which was necessary along with the addition of the electrically conducting material when acetylene black or synthetic graphite was used as was the practice in the past can be reduced with the net result that the capacity of the positive electrode is increased and the internal resistance is lowered.

This invention is described below through a practical example.

Positive electrode: 100 parts by weight of activated manganese dioxide heat treated at 350-430°C, 10 parts by weight of expanded graphite to serve as electrical conductor, and 2 parts by weight fluorinated resin powder to serve as binder were mixed, and 50 g of this mixture was mixed thoroughly for 30 minutes in a mortar to prepare the positive electrode bobbin. This mixture was then formed into 20 ϕ diameter and 1.2 mm thickness buttons under a forming pressure of 2 tons/cm² after which the buttons were given a heat treatment at 300°C to finish the positive electrode.

Negative electrode: Lithium rolled plate of roughly 0.5 mm thickness was punched out into 20 ϕ diameter disks for use as the negative electrode.

Electrolyte solution: Lithium perchlorate was dissolved at a concentration of 1 M in an equal volume mixture of solvents such as propylene carbonate and 1,2-dimethoxymethane, and this electrolyte solution was used together with an unwoven polypropylene fabric separator.

Figure 2 is a vertical cross section of an outer diameter 25 ϕ and 2.8 mm height battery assembled using the various elements of this invention in which (1) is the positive electrode can, (2) is the negative electrode can, (3) is the positive electrode placed at the inside surface of positive electrode can (1), (4) is the negative electrode placed against the inner surface of negative electrode can (2) and separated from the can by negative electrode collector (41), (5) is the separator, and (6) is the insulating packing which electrically insulates the positive and negative cans from each other.

Next, a study was made to establish the superiority of the battery of this invention by comparison with a battery using acetylene black as the electrically conducting material in which the positive electrode was prepared from 100 parts by weight manganese dioxide, 10 parts by weight acetylene black, and 6 parts by weight fluorinated resin powder other than which all other conditions were the same as in this first battery. Because of the

poor forming property of the acetylene black used as electrically conducting material in this comparative battery, there was need to add at least 6 parts by weight binder in order to assure mechanical strength.

Figure 5 is a diagram of the discharge characteristics on 5.6 K Ω constant load discharge at room temperature of the battery of this invention (A₁) and the comparison battery (B) while Fig. 4 shows the low temperature discharge characteristic at -20°C with 12 K Ω constant load.

Example 2

Batteries were assembled in which the weight fractions of the various components of the battery of Example 1 were varied in the manner shown in the table below.

Table

(1) 電池	(2) 正極活性物質 (二酸化マンガン)	(3) 導電剤 (膨張黒鉛)	(4) 接着剤 (フッ素樹脂)
A ₁	(5) 100 重量部	(5) 10 重量部	(5) 2.0 重量部
A ₂	100 "	10 "	0.5 "
A ₃	100 "	10 "	1.0 "
A ₄	100 "	10 "	1.5 "
A ₅	100 "	10 "	4.0 "

- Key: 1. Battery
 2. Positive electrode active material (manganese dioxide)
 3. Electrical conductor (expanded graphite)
 4. Binder (fluorinated resin) 5. --- parts by weight

The 560 K Ω constant load discharge characteristics of the various batteries of this invention from example 2 and the comparison battery are shown in Fig. 5, and it can be seen that the battery containing 0.5-2.0 parts by weight electrically conducting material displayed particularly good characteristic.

Example 3

Positive electrode: A 100 parts by weight lot of manganese dioxide activated by heat treatment at 350-430°C and 10 parts by weight of expanded graphite as electrical conductor were mixed, and 1 kg of this positive

electrode bobbin material was mixed with 350 cc of aqueous 7% polyvinyl alcohol solution to prepare a paste.

This paste was coated on the surface of a positive electrode collector made of stainless steel, the coating was allowed to dry, and the dry product was punched out into 20 ϕ diameter buttons to be used as the positive electrode. The rest of the assembly was the same as in the procedure of Example 1 for the assembly of battery (A₆).

The 560 K Ω constant load discharge characteristics of battery (A₆) of this invention from Example 3 and comparative battery (B) determined at room temperature are shown in Fig. 6.

As described in detail above, this invention relates to a nonaqueous electrolyte solution battery with a negative electrode using a light metal such as lithium or sodium as the active material, a positive electrode with a metal oxide, sulfide, or halogen compound active material, and a nonaqueous electrolyte solution comprised of at least one solvent and one solute in which the electrically conducting material of the positive electrode is expanded graphite which enables spectacular improvement in the battery properties and which introduces extremely high industrial value.

4. Brief Explanation of Figures

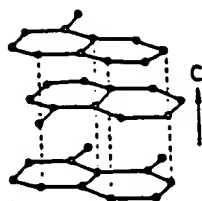
Figure 1 is a crystal structural diagram of expanded graphite, Fig. 2 is a vertical cross section of a battery of this invention, and Fig. 3 through Fig. 6 are discharge property diagrams of batteries of this invention and a comparative battery.

(1): positive electrode can, (2): negative electrode can, (3): positive electrode, (4): negative electrode, (5), separator, (6): insulating packing.

Applicant Sanyo Electric Co., Ltd.

Agent Attorney Shizuo Sano

Figure 1



Figur 2

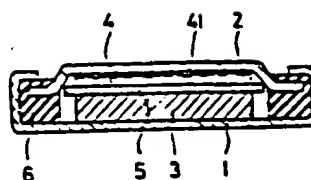
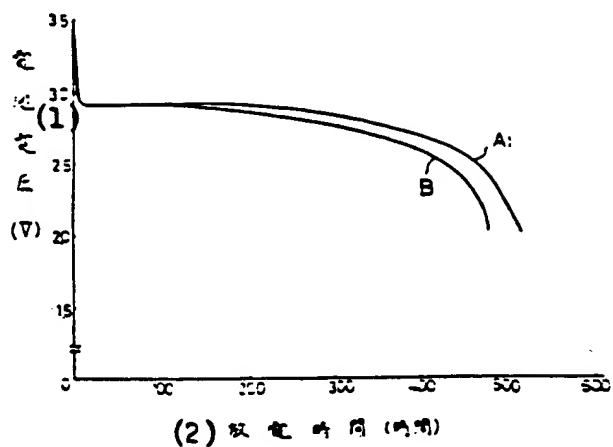
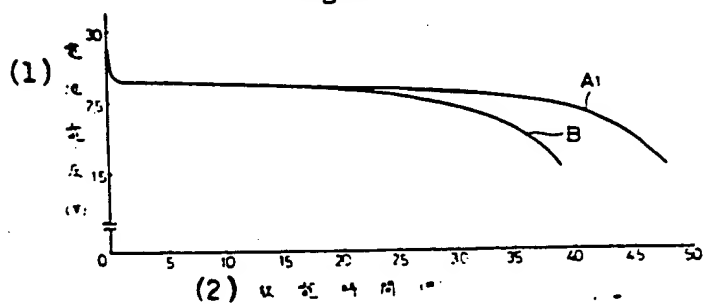


Figure 3



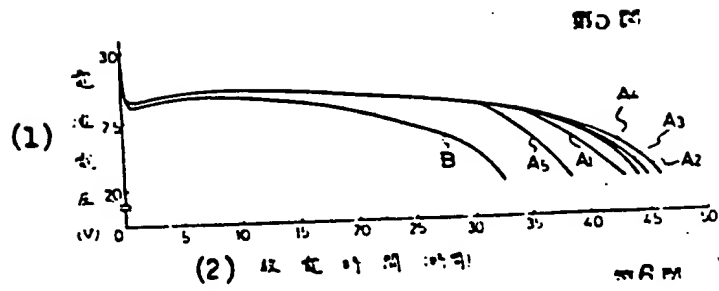
Key: 1. Battery voltage (V) 2. Discharge time (hr)

Figure 4



Key: 1. Battery voltage (V) 2. Discharge time (hr)

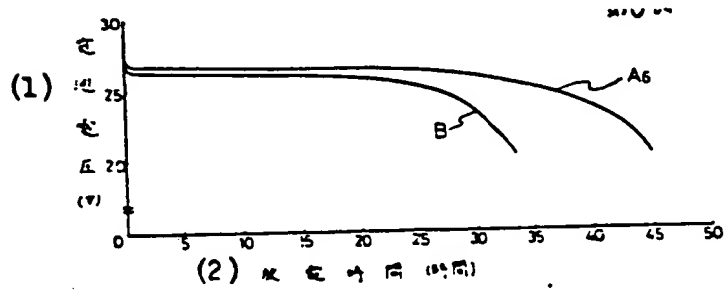
Figure 5



Key: 1. Battery voltage (V)

2. Discharge time (hr)

Figure 6



Key: 1. Battery voltage (V)

2. Discharge time (hr)

